Breaking of time-reversal symmetry probed by optical second-harmonic generation

R. Stolle, K. J. Veenstra, F. Manders, and Th. Rasing
Research Institute for Materials, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands

H. van den Berg
Siemens AG, D-91052 Erlangen, Germany

N. Persat
IPCMS-GEMME, UMR 46 CNRS-ULP, 23 rue du Loess, 67037 Strasbourg, France
(Received 18 November 1996)

We have studied both the phase and the intensity of the magnetization-induced second-harmonic generation from a Rh/Co/Cu multilayer on an SiO_2 substrate. In selected polarization combinations we observe, respectively, a 180° and no phase shift of the SH signal upon sign reversal of the magnetization. This is a direct manifestation of the time-reversal symmetry breaking by magnetization. [S0163-1829(97)51208-2]

The magnetism of surfaces, thin films, and multilayers attracts a great deal of interest not only from a technological but also from a scientific point of view.[1] Recently, it has been shown that magnetization-induced second-harmonic generation (MSHG) can provide valuable information about these systems due to its intrinsic surface sensitivity.[2] MSHG has been used to study surface magnetism,[3] e.g., of Co and Fe films on Cu,[4] and the imaging of domains and domain walls in magnetic garnet films.[5] Apart from its interface sensitivity, MSHG is characterized by its huge magneto-optical effects: nonlinear Kerr rotation close to 90° has been observed,[6–8] as well as magnetization-induced changes of the order of 100%.[9] Both of these effects are due to a simultaneous breaking of inversion symmetry (at interfaces) and time-reversal symmetry (by magnetization $\vec{M}$).

As shown by Ru-Pin Pan *et al.*,[10] the presence of $\vec{M}$ leads to a magnetization-dependent nonlinear optical susceptibility tensor, $\chi^{(2)}$, with elements being either purely symmetric or antisymmetric with respect to $\vec{M}$. That is, upon reversal of the direction of $\vec{M}$ the $\chi^{(2)}$ components either remain unchanged or they undergo a π phase shift, respectively. Though the consequences of this phase shift have been observed in the already mentioned nonlinear magneto-optical effects, the existence of purely symmetric and antisymmetric susceptibility tensor elements has never directly been observed experimentally. In this paper we present a direct observation of the effects of this breaking of the time-reversal symmetry by measuring both the phase and the intensity changes of the second-harmonic radiation in selected polarization combinations upon sign reversal of the magnetization $\vec{M}$.

In the electric dipole approximation the nonlinear polarization $P(2\omega)$ induced by an incident fundamental laser field $E(\omega)$ can be written as

$$P_i(2\omega)=\chi_{ijk}^{(D)}E_j(\omega)E_k(\omega) \tag{1}$$

with $\chi_{ijk}^{(D)}$ being the nonlinear optical susceptibility tensor. This third-rank susceptibility tensor is zero in any centrosymmetric medium. However, centrosymmetry is necessarily broken at interfaces resulting in the high surface and interface sensitivity of SHG.[11] Note that the magnetization of a material does not break the centrosymmetry due to the axial character of the magnetization.

In the case of an "isotropic" interface with $C_{\infty,v}$ symmetry, defined by the x,y plane with x being in the plane of incidence and with a magnetization parallel to x ("longitudinal configuration," see Fig. 1), the nonlinear susceptibility is given by[10]

$$\chi_{ijk}^{(D)}(\vec{M}) = \begin{pmatrix} 0 & 0 & 0 & 0 & \chi_{xzx}^{(even)} & \chi_{xyx}^{(odd)} \\ \chi_{yxx}^{(odd)} & \chi_{yyy}^{(odd)} & \chi_{yzz}^{(odd)} & \chi_{yzy}^{(even)} & 0 & 0 \\ \chi_{zxx}^{(even)} & \chi_{zyy}^{(even)} & \chi_{zzz}^{(even)} & \chi_{zyz}^{(odd)} & 0 & 0 \end{pmatrix}. \tag{2}$$

This magnetization-dependent susceptibility tensor consists of components which are either even (symmetric), $\chi_{ijk}^{(even)}(\vec{M})$, or odd (antisymmetric), $\chi_{ijk}^{(odd)}(\vec{M})$, in magneti-

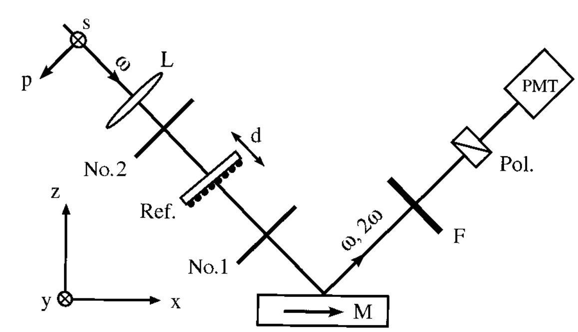

FIG. 1. Experimental setup. When the SH intensity from the sample is measured, the RG-630 glass filter (absorbs the second-harmonic radiation) is placed at position No. 1. To measure the interference, the filter is placed at position No. 2. The angle of incidence was 45°.

TABLE I. Comparison of theory and experiment: phase difference $\Delta\Phi$ and relative magnetic effect ρ in the SH signal upon sign reversal of magnetization in selected polarization combinations.

Polarization	$\chi^{(2)}$ components	Symmetry	$\Delta\Phi$		ρ	
			Expt.	Theory	Expt.	Theory
$s_{in}-p_{out}$	$\chi_{zyy}^{(even)}$	even	$0°\pm5°$	$0°$	$\lesssim1\%$	0
$s_{in}-s_{out}$	$\chi_{yyy}^{(odd)}$	odd	$179°\pm5°$	$180°$	$\lesssim1\%$	0
$p_{in}-p_{out}$	$\chi_{zxx}^{(even)}$, $\chi_{xzx}^{(even)}$, $\chi_{zzz}^{(even)}$	even	$2°\pm5°$	$0°$	$\lesssim1\%$	0
$p_{in}-s_{out}$	$\chi_{yxx}^{(odd)}$, $\chi_{yzz}^{(odd)}$	odd	$185°\pm5°$	$180°$	$\lesssim1\%$	0
$s_{in}-45°_{out}$	$\chi_{yyy}^{(odd)}$, $\chi_{zyy}^{(even)}$	·/·	$30°\pm5°$	·/·	$\approx50\%$	·/·

zation, i.e., upon sign reversal of the magnetization the odd components change sign whereas the even components remain unchanged.

In this longitudinal configuration one can find polarization combinations of the incoming fundamental beam and the generated second-harmonic beam with the underlying tensor components being either purely even or purely odd (see Table I). In the even configurations, $s_{in}-p_{out}$ and $p_{in}-p_{out}$, both the phase and the magnitude of the generated second-harmonic radiation remain unchanged upon sign reversal of the magnetization, whereas in the odd combinations, $s_{in}-s_{out}$ and $p_{in}-s_{out}$, the SH radiation undergoes a π phase shift. In most experiments this phase information is lost, since only intensities are measured. Therefore, MSHG effects have been observed only in a more indirect way through interference effects between odd and even terms, i.e., in a polarization combination corresponding to a sum of even and odd tensor components, as in the case of $s_{in}-45°_{out}$ However, one can directly measure phase shifts of the SH signal by making use of an external SHG source with an adjustable relative phase.[12–14]

We studied MSHG in the reflection geometry on a magnetic multilayer system, consisting of a Co film (thickness 50 nm), covered with a 1.5 nm Rh film deposited by dc magnetron and rf diode sputtering, respectively. As a substrate we used a (100) silicon wafer, with a thermal oxide layer of about 500 nm, and a Cu buffer of 30 nm. Both targets were equipped with screens for getting uniformity of the layer thickness better than 1%. The base pressure was 5×10^{-8} Torr and the Ar pressure was 5 mTorr.

For the SHG experiments we used the output of a Ti:Sapphire laser operating at a wavelength of 840 nm with a repetition rate of 82 MHz and a pulse width of 100 fs. The average power at the sample was about 260 mW, with a spot diameter of approximately 200 μm. The magnetization was parallel to the x direction. Using a Babinet-Soleil compensator and an analyzing polarizer we were able to choose any combination of linear polarization for the fundamental and the second-harmonic beam (see Fig. 1).

The intensity and phase of the second-harmonic radiation generated by the sample were obtained in two different kinds of measurements. The SH *intensity* is measured by placing the RG-630 filter that blocks the radiation at the second harmonic frequency at position No. 1. If the filter is placed at position No. 2 instead of No. 1, the *phase* of the second-harmonic light can be determined by employing a SH interference technique originally introduced by Chang *et al.*[12] The SH signal of the sample is superimposed by that of a second (reference) SHG source, and interference is observed by measuring the total SH signal upon variation of the optical phase delay Φ between these two SH sources. As the second SH source we used a glass slide covered on one side by a thin poled polymer film with a high second-order nonlinearity. We checked that this sample does not affect the linear polarization of the transmitted fundamental beam. By translating the reference source along the path of the beam by d, we introduced an extra optical phase delay $\delta\Phi=(4\pi\Delta n/\lambda)d$, resulting in a cosinelike interferogram of the total SH signal:

$$I_{2\omega,tot}(d)=I_{2\omega,s}+I_{2\omega,r}+2\sqrt{I_{2\omega,s}I_{2\omega,r}}\cos(\delta\Phi+\Phi), \quad (3)$$

where $I_{2\omega,s}$ and $I_{2\omega,r}$ indicate the SH signal generated by the sample and the reference, respectively. Δn is the dispersion of the ambient air and λ is the fundamental wavelength. Since the fundamental beam was focused on the sample, the reference signal depends on the position d with respect to the focus position d_0 as $I_{2\omega,r}(d)\propto1/(d-d_0)^2$, and therefore the interference pattern has not a perfect cosine form[15,16] but is given by the expression

$$I_{2\omega,tot}(d)=I_{2\omega,s}+I_{2\omega,r}(d)+2\alpha\sqrt{I_{2\omega,s}I_{2\omega,r}(d)} \times\cos[(4\pi\Delta n/\lambda)d+\Phi] \quad (4)$$

with the coherence parameter α describing the spatial and temporal coherence of the laser,[17] and the phase Φ being the sum of the phase shifts introduced by the sample and the reference. For a fundamental radiation of 840 nm, the dispersion of air at room temperature and normal atmospheric conditions is[18] $\Delta n=n(840\ \text{nm})-n(420\ \text{nm})\approx6.5\times10^{-6}$, resulting in a periodicity of the interferogram of approximately 65 mm.

In order to determine the magnetic saturation field, we measured the MSHG hysteresis in the polarization com-

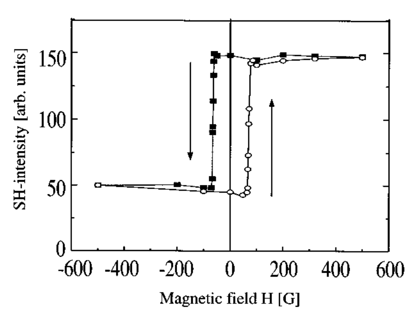

FIG. 2. The $s_{in}-45°_{out}$ second-harmonic intensity generated by the sample as a function of the applied magnetic field.

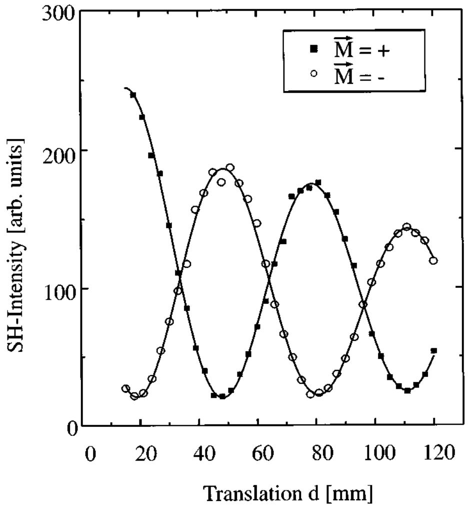

FIG. 3. Interference patterns for the SHG for opposite magnetizations of the sample in the odd $p_{in}-s_{out}$ configuration and best fits to (4). The phase difference was found to be $\Delta\Phi=(185\pm5)°$.

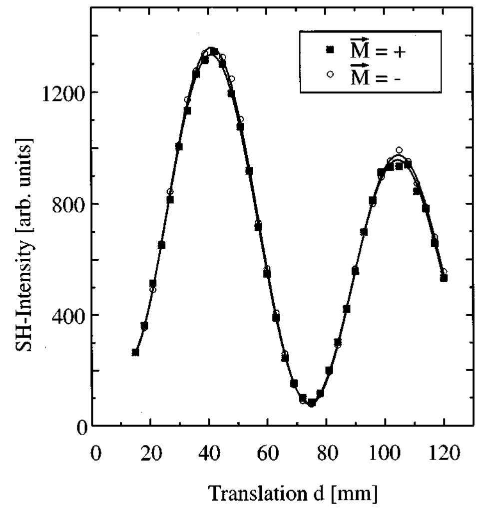

FIG. 4. Interference patterns for the SHG for opposite magnetizations of the sample in the even $s_{in}-p_{out}$ configuration and best fits to (4). The phase difference was found to be $\Delta\Phi=(0\pm5)°$.

bination $s_{in}-45°_{out}$ (Fig. 2), since in this configuration we probe a sum of one odd and one even susceptibility component (cf. Table I). The magnetic-induced changes in SH intensity are very high: the relative magnetic effect $\rho=I(2\omega,M^+)-I(2\omega,M^-)/[I(2\omega,M^+)+I(2\omega,M^-)]$ is about 50%.

The interference patterns obtained in the odd $p_{in}-s_{out}$ polarization combination upon sign reversal of the magnetic field are shown in Fig. 3. The data can be perfectly fitted by (4), resulting in a phase difference $\Delta\Phi=\Phi(M^+)-\Phi(M^-)=(185\pm5)°$. This value as well as the obtained relative magnetic effect in the SH intensity of $\rho\lesssim1\%$ is in excellent agreement with the theory that predicts a π shift of the harmonic radiation. Figure 4 depicts the results of a phase measurements in the even $s_{in}-p_{out}$ combination. The phase difference was $\Delta\Phi=(0\pm5)°$, and the relative magnetic effect was $\rho\lesssim1\%$, both again in good agreement with the phenomenological model.[10] Table I shows the experimental results for all selected polarization combinations.

Though the present analysis was done for electric dipolar response terms $\chi^{(D)}_{ijk}$, it can simply be shown that, as long as the surface has one mirror plane, this odd/even division is a general rule. This means that it also holds for, e.g., electric quadrupolar or magnetic dipolar sources.[19,20] Moreover, any possible linear magneto-optical effects (Kerr and Faraday) on the incident and outgoing waves do not affect the phase shifts considered in this paper.[19]

In conclusion we have demonstrated that the presence of a time-reversal symmetry breaking magnetization induces purely odd and even elements of the nonlinear optical susceptibility tensor. By studying both phase and intensity of MSHG from an isotropic magnetic multilayer in the longitudinal configuration, this odd/even effect could directly be demonstrated by the observation of a 180°, zero phase shift of the SH radiation upon sign reversal of the longitudinal applied magnetic field.

We would like to thank A. V. Petukhov for stimulating discussions. Part of this work was supported by the Stichting Fundamenteel Onderzoek der Materie (FOM) and by the TMR network NOMOKE. One of us (R.S.) was supported by the TMR (Grant No. ERBFMBICT 960837).

[1] L. Falicov *et al.*, J. Mater. Res. **5**, 1299 (1990).
[2] J. Reif, J. C. Zink, C.-M. Schneider, and J. Kirschner, Phys. Rev. Lett. **67**, 2878 (1991).
[3] W. Hübner and K. H. Bennemann, Phys. Rev. B **40**, 5973 (1989).
[4] H. A. Wierenga *et al.*, Phys. Rev. Lett. **74**, 1462 (1995).
[5] A. Kirilyuk *et al.*, J. Magn. Soc. Jpn. **20 (S1),** 361 (1996).
[6] M. Groot Koerkamp and Th. Rasing, J. Magn. Magn. Mater. **156**, 213 (1996).
[7] J. Reif, C. Rau, and E. Matthias, Phys. Rev. Lett. **71**, 1931 (1991).
[8] B. Koopmans, M. Groot Koerkamp, Th. Rasing, and H. van den Berg, Phys. Rev. Lett. **74**, 3692 (1995).
[9] R. Vollmer, M. Straub, and J. Kirschner, J. Magn. Soc. Jpn. **20 (S1),** 29 (1996).
[10] R.-P. Pan, H. D. Wei, and Y. R. Shen, Phys. Rev. B **39**, 1229 (1989).
[11] Y. R. Shen, *The Principles of Nonlinear Optics* (Wiley, New York, 1984).
[12] R. K. Chang, J. Ducuing, and N. Bloembergen, Phys. Rev. Lett. **15**, 6 (1965).
[13] R. Stolle, G. Marowsky, E. Schwarzberg, and G. Berkovic, Appl. Phys. B **63**, 491 (1996).
[14] R. Superfine, J. H. Huang, and Y. R. Shen, Opt. Lett. **15**, 1276 (1990).
[15] R. Stolle *et al.*, Langmuir **11**, 3251 (1995).
[16] K. Kemnitz *et al.*, Chem. Phys. Lett. **131**, 285 (1986).
[17] G. Berkovic and E. Schwarzberg, Appl. Phys. B **53**, 333 (1991).
[18] *CRC Handbook of Chemistry and Physics*, edited by D. R. Lide (CRC Press, Boston, 1991).
[19] A. V. Petukhov and Th. Rasing (unpublished).
[20] H. A. Wierenga, Ph.D. thesis, University of Nijmegen, 1995 (unpublished).